Effect of Substituents on the Rate of Oxidation of Anilines with Peroxomonosulfate Monoanion ($HOOSO_3^-$) in Aqueous Acetonitrile: A Mechanistic Study

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ABSTRACT: Mechanistic studies on the oxidation of 18 *meta-, para-*, and *ortho*-substituted anilines (Ans) by $HOOSO_3^-$ in aqueous acetonitrile medium have been performed. The reaction can be characterized by the experimental rate equation,

$$\frac{-d[HSO_5^-]}{dt} = k[An][HSO_5^-]$$

The addition of p-toluenesulfonic acid (TsOH) retards the reaction. The increase in the reactivity of anilines as the medium is made more aqueous is interpreted. The reaction is enhanced by electron-donating groups on the amine in the series consistent with the rate-limiting nucleophilic attack of the amine on the persulfate oxygen. The proposed mechanism involves the conversion of phenylhydroxylamine to nitrosobenzene in a fast step. The ESR study reveals the absence of free radicals in the reaction. Various attempts have been made to analyze the

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experimental rate constants in terms of LFER plots. Improved correlations are obtained with σ^- values and the σ^- form of the Yukawa–Tsuno equation. Int J Chem Kinet 37: 649–657, 2005

INTRODUCTION

The oxidation of amines to their oxygenated derivatives is an important industrial reaction and particularly, the reactions of aromatic amines by peroxidic reagents have received considerable attention. Recently, we embarked on the investigation of the kinetics of reaction involving substituted anilines and peroxomonosulfate monoanion with the view of probing their mechanisms. Thus far, the kinetics of oxidation of substituted anilines by $HOOSO_3^-$ in basic medium [1] and Ru(III)-inhibited oxidation in acidic solution [2] (pH $\approx$ 2.6) have been examined. Abdul and Maruthamuthu [3] have reported the oxidation of anilines by $HOOSO_3^-$ in aqueous acetic acid medium.

The solvent plays an important role in deciding the reaction mechanism. In aqueous acetic acid medium [2,3], no simple Hammett relation was found for the substituent effects and the lack of LFER was explained. In aqueous methanol medium [1], the highlight of the study was the opposite curvatures observed in nonlinear Hammett plots for the rate of decomposition (k) and the equilibrium constant, K, being concave downward and upward, respectively. In this study, based on the kinetic data, we have tried to ascertain the structure-reactivity relationship in aqueous acetonitrile medium. In contrast to previously described results, we have found that, in aqueous MeCN, the conversion of aromatic amines (Ans) to nitroso products obeys the linear free energy relationship (LFER).

RESULTS AND DISCUSSION

A first-order dependence on $[HOOSO_3^-]$ was evidenced by the linear semilogarithmic plots of titer versus time. The first-order plots show curvature after 60% conversion (Fig. 1) of $HOOSO_3^-$ which may be due to the effect of the product formed. The curvature in the first-order plots seems to be quite common in the oxidations by peroxomonosulfate anion [4–6]. The plot of k_{obs} as a function of the concentration of aniline at constant temperature is linear with a zero intercept ($r = 0.998$; $s = 0.121$). The kinetic data are summarized in Table I. The reaction can be characterized by the rate equation (1),

$$\frac{-d[HSO_5^-]}{dt} = k[An][HSO_5^-] \qquad (1)$$

The insensitivity of rates to added acrylonitrile as shown in Table II rules out a mechanism involving homolytic fission of the peroxide bond. The reactivity of anilines increases as the amount of water in the solvent is increased (Table I). This probably indicates that the transition state is more polar than the reactants in the initial state. A linear plot of log k_{obs} versus D^{-1} (Fig. 2) ($r = 0.980$; $s = 0.107$) with a negative slope suggests that there is an involvement of negative ion in the rate-limiting step. The rate coefficients analyzed with the Grunwald–Winstein [7] equation (2) (Fig. 3), result in

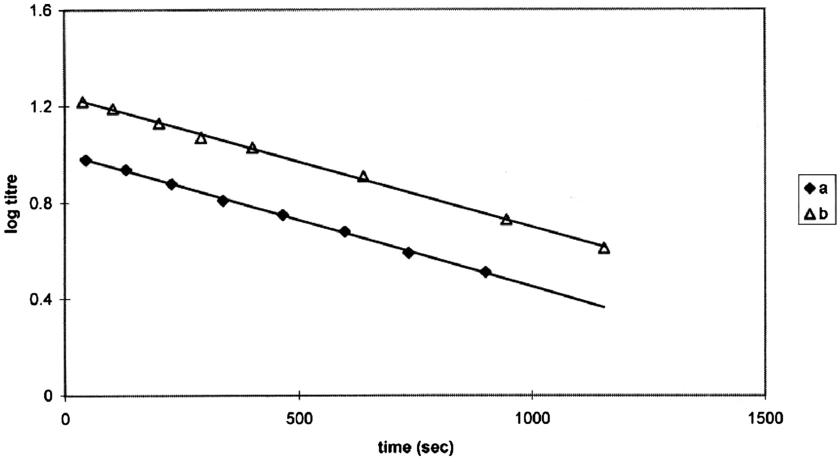


Figure 1 First-order plots for the reaction of aniline with oxone at 303 K. (a) $[Oxone]_0 = 0.86 \times 10^{-3}$ mol dm^{-3}. (b) $[Oxone]_0 = 1.55 \times 10^{-3}$ mol dm^{-3}.

Table I Effect of Reactants on the Rate of Oxidation of Aniline with Oxone at 303 K

10^3[Oxone]$_0$ (mol dm^{-3})	10^2[Aniline]$_0$ (mol dm^{-3})	D^a	$10^3 k_{\mathrm{obs}}$ (s^{-1})
0.860	4.00	44.08	1.30
1.15	4.00	44.08	1.25
1.55	4.00	44.08	1.22
2.01	4.00	44.08	1.11
1.15	2.00	44.08	0.58
1.15	3.20	44.08	1.02
1.15	4.00	44.08	1.25
1.15	6.00	44.08	1.91
1.15	8.00	44.08	2.56
1.15	14.0	44.08	5.07
1.15	4.00	57.00	5.61
1.15	4.00	52.69	3.57
1.15	4.00	42.38	2.02
1.15	4.00	44.08	1.25
1.15	4.00	39.77	0.360

[a] Dielectric constant values are calculated from the values of pure solvents.

a curvature

$$\log k = \log k_o + mY \tag{2}$$

Here Y is the quantity which measures the ionizing power of the solvent (Y_{OTS} values are used) and $m \approx 0.4$. Less satisfactory fits with Eq. (2) suggested an $\mathrm{S_N2}$ type reaction [8]. The small value of m certainly suggests that the charge separation is not large in the passage from the ground state to the transition state. The small m value is comparable with the values observed in bimolecular substitution reactions [7,9].

The change in ionic strength (Table II) showed a small increase in k_{obs} with increase in the ionic strength.

Table II Effect of Sodium Perchlorate, TsOH, and Acrylonitrile on the Reaction Rate at 303 K

10^2[NaClO$_4$] (mol dm^{-3})	10^2[TsOH] (mol dm^{-3})	10^3[Acrylonitrile] (mol dm^{-3})	$10^3 k_{\mathrm{obs}}$ (s^{-1})
–	–	–	1.25
2.64	–	–	1.50
5.00	–	–	1.72
7.90	–	–	1.90
10.20	–	–	2.13
–	0.00	–	1.25
–	0.56	–	0.79
–	1.12	–	0.64
–	2.24	–	0.49
–	–	5.0	1.23
–	–	10.0	1.22
–	–	16.0	1.20
–	–	20.0	1.25

[Aniline]$_0$ = 4.00×10^{-2} mol dm^{-3}; [Oxone]$_0$ = 1.15×10^{-3} mol dm^{-3} Acetonitrile: H_2O = 80:20 (v/v).

D_2O has no significant effect on the rate of conversion as shown in Table III. The lack of solvent isotope effect excludes the rate-controlling participation of water, as a proton transfer agent [10]. In the present investigations, since the solvent composition variation is very small, a proton transfer process is not completely ruled out.

p-Toluenesulfonic acid (TsOH) retards the reactivity of anilines significantly (Table II). The pseudo-first-order rate constants decrease from 1.25×10^{-3} s^{-1} to 0.49×10^{-3} s^{-1} by adding 2.24×10^{-2} mol dm^{-3} of TsOH. This observation suggests that the free availability of the aniline lone pair facilitates the oxidation. It appears that the ionization state of the amine is important. It seems quite unlikely that the addition of acid (ca. 2×10^{-2} mol dm^{-3}) is changing the nature of the oxidizing species.

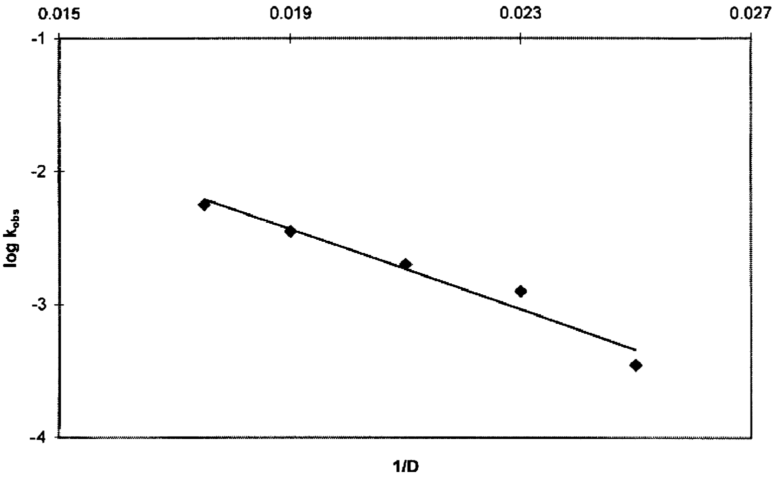


Figure 2 A plot of log k_{obs} versus $1/D$.

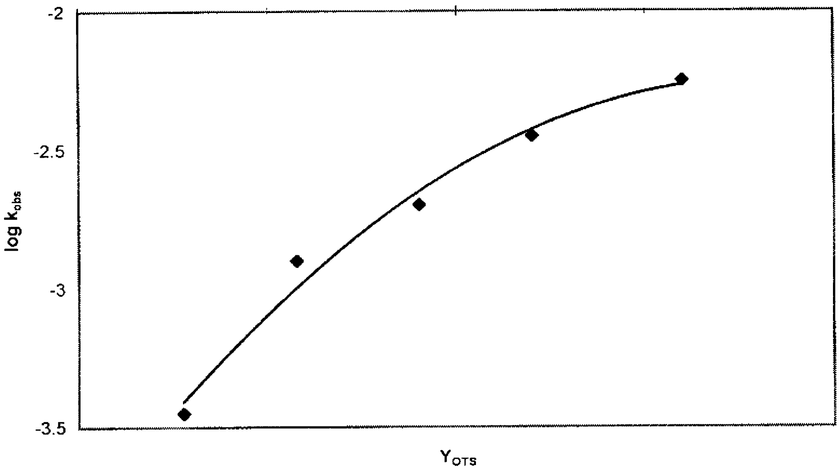


Figure 3 A plot of log k_{obs} versus Y_{OTS}.

Effect of Substituents

Substituent effects are used as probes of the reaction mechanisms of aromatic compounds. The effect of substituents on aniline reactivity has been investigated by employing 18 *meta-*, *para-*, and *ortho*-substituted anilines. Generally, from the results it is evident that electron-releasing substituents accelerate the rate while electron-withdrawing ones retard the reactivity. The rate coefficients and activation parameters evaluated from the Eyring plots of ln (k/T) versus $1/T$ are listed in Table IV.

The Hammett equation is an empirical relationship for correlating structure and reactivity. The rate coefficients of the members of the amine series are linearly related to the respective σ values. Experimental data are better correlated with the Hammett $\rho\sigma$ relationship (Fig. 4) ($r = 0.949$; $s = 0.256$) rather than the Brown–Okamoto $\rho\sigma^+$ relationship (Fig. 5) ($r = 0.923$; $s = 0.313$) for the substituents in the *meta-* and *para*-positions of the benzene ring. In the case of *para*-substituents, only the correlation of the rate constants with σ/σ^+ is much better ($r \approx 0.977$; $s \approx 0.218$). The reaction constant values are listed in Table V. The ρ values suggest an electron-deficient transition state.

A slight deviation is observed in the Hammett plot for the m-NO_2 substituent (no. 11). Instead of the Hammett value, if the σ_R^- value (0.46) based on the ionization of anilinium ions in water at 25°C is applied, then the m-NO_2 substituent falls on the Hammett line. We have tried to express the kinetic data in terms of Yukawa–Tsuno equation [11], Eq. (3), taking into account an exalted resonance contribution

$$\log(k/k_o) = \rho(\sigma + r^+ \Delta\sigma_R^+) \qquad (3)$$

where r^+ is a constant depending on the resonance effect in the reaction, and $\Delta\sigma_R^+$ measures the capacities of substituents to supply electrons by resonance. Figures 6 and 7 show results with r^+ equal to 0.074 and 0.254, respectively. The positive r^+ value shows that the transition state is stabilized by additional resonance between positively charged reaction center and electron-releasing substituents. As is clear in these figures the correlation does not improve much ($r = 0.950$; $s = 0.259$). The effect of the *para*-substituents on the first-order rate coefficients is well described by Yukawa–Tsuno equation as shown in Table VI ($R \approx 0.988$; $s \approx 0.144$).

The ratio of rate coefficients of *para-* and *ortho*-substituted anilines is >1 (Table VII). This observation suggests a significant steric hindrance in the $HOOSO_3^-$ oxidations of anilines. However, the general adherence to the Hammett equation for the *ortho*-substituted anilines listed shows that the steric effect is not too large. These contrasting observations reflect small but significant steric effect in the reactivity. Analysis of the rate coefficients (at 303 K) with Charton's equation [12] further reveals that the coefficient of the steric term is

Table III Effect of D_2O on the Reaction Rate

% Solvent Acetonitrile : H_2O : D_2O	$10^3 k_{\mathrm{obs}}$ (s^{-1})
80 : 20 : 00	1.25
80 : 15 : 05	1.23
80 : 10 : 10	1.22
80 : 05 : 15	1.20

$[\mathrm{Aniline}]_0 = 4.00 \times 10^{-2}$ mol dm^{-3}; $[\mathrm{Oxone}]_0 = 1.15 \times 10^{-3}$ mol dm^{-3}.

Table IV Rate Constants and Activation Parameters for the Oxidation of Anilines with Oxone in Aqueous Acetonitrile Medium

		$k_{obs}10^3$ (s^{-1})			$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta G^{\neq}$(30°)		
No.	Aniline	20°C	30°C	40°C	(kJ mol^{-1})	(J K^{-1} mol^{-1})	(kJ mol^{-1})	*r*	*s*
1	H	0.67	1.25	1.97	38.2	175.0	93.0	0.998	0.051
2	*p*-CH_3	1.20	2.11	3.97	42.7	155.2	89.7	0.999	0.042
3	*p*-OCH_3	2.27	4.28	7.83	44.6	143.2	88.0	0.999	0.005
4	*p*-Cl	0.34	0.54	1.25	59.9	110.0	93.2	0.999	0.021
5	*p*-Br	0.30	0.52	0.81	35.5	191.1	93.4	0.999	0.022
6	*p*-NO_2	0.006	0.01	0.02	40.0	207.9	103.0	0.997	0.017
7	*p*-COOH	0.03	0.05	0.13	59.0	132.0	99.0	0.994	0.081
8	*m*-CH_3	0.63	1.16	1.95	40.9	166.7	91.4	0.999	0.028
9	*m*-OCH_3	0.43	0.72	1.12	33.6	194.5	92.5	0.999	0.019
10	*m*-Cl	0.07	0.13	0.25	48.1	161.0	96.8	0.999	0.018
11	*m*-NO_2	0.05	0.10	0.16	42.9	181.0	97.7	0.991	0.105
12	*o*-CH_3	0.46	0.71	1.43	40.3	171.6	92.3	0.986	0.122
13	*o*-OCH_3	1.53	3.15	5.96	49.2	130.7	88.8	0.999	0.017
14	*o*-F	0.06	0.11	0.19	43.6	177.4	97.3	0.998	0.004
15	*o*-Cl	0.02	0.04	0.08	43.0	186.3	99.5	0.991	0.106
16	*o*-I	0.01	0.03	0.05	51.6	162.9	100.9	0.998	0.061
17	*o*-COOH	0.03	0.04	0.09	44.2	182.3	99.4	0.995	0.078
18	*o*-NO_2	0.004	0.007	0.01	40.1	212.0	104.3	0.999	0.030

$[\text{Amine}]_0 = 4.00 \times 10^{-2}$ mol dm^{-3}, $[\text{Oxone}]_o = 1.15 \times 10^{-3}$ mol dm^{-3}.

small but significant (Eqs. (3) and (4)).

$$\log k = \alpha\sigma_I + \beta\sigma_R + \varphi\nu + h \qquad (4)$$

$$\log k = -2.18\sigma_I - 0.81\sigma_R - 0.5\nu - 2.92 \qquad (5)$$

$(100R = 90; \text{SE} = 0.53, n = 8)$

(σ_R^- values used in the correlation;

$-NO_2$ and $-COOH$ planar)

Also, the localized effect predominance is clearer from the high value of the σ_I coefficient.

Mechanism

The peroxomonosulfate anion exists [13] as HSO_5^- in polar solvents. Many peroxyanions are effective nucleophiles, while HSO_5^- is a very weak nucleophile [9]. In spite of the fact that free radicals can arise from

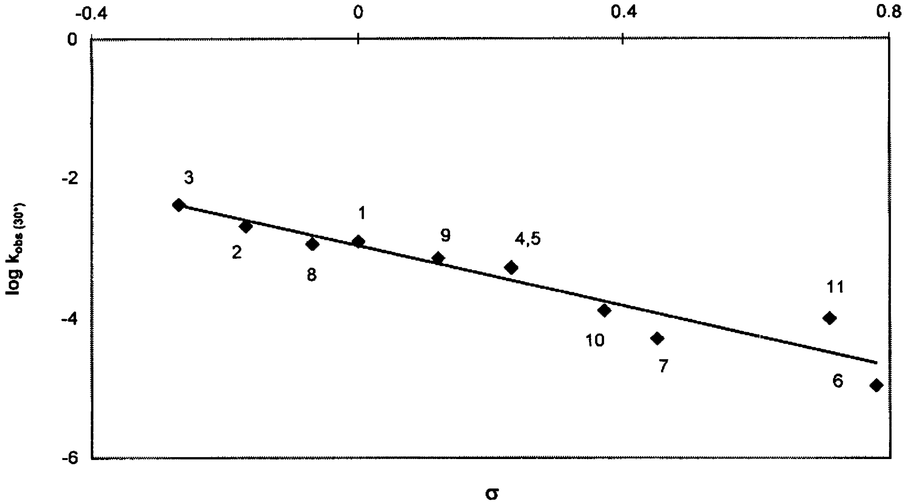


Figure 4 The Hammett plot (numbered as in Table IV).

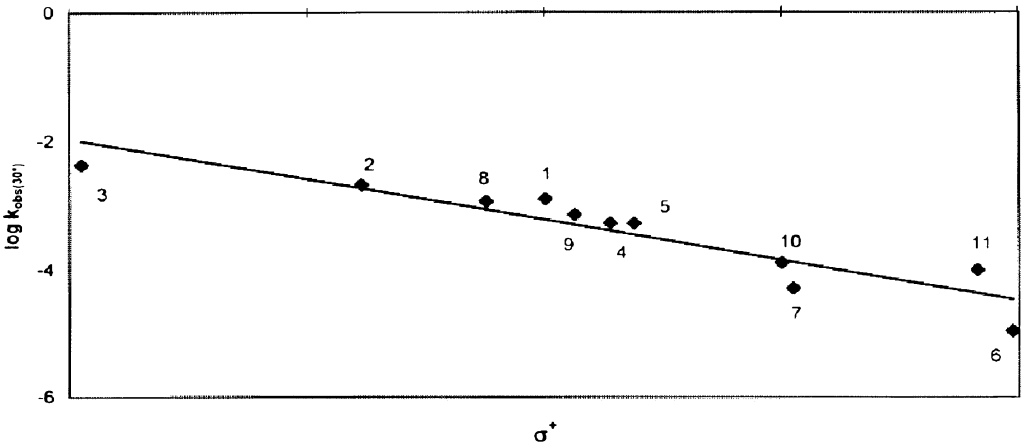


Figure 5 Brown–Okamoto plot (numbered as in Table IV).

the facile homolysis of the oxygen—oxygen bond [14], an ionic mechanism is favored in certain reactions involving oxidations by peroxides. In the present investigation, no observed polymerization in the presence of acrylonitrile rules out a free radical process. The ESR study indicates the absence of free radical processes during and after the reaction. Negative reaction constant (ρ) values suggest a bimolecular process that involves the nucleophilic attack of aniline on the peroxidic oxygen. A type of transition state with a fully developed positive charge on the nitrogen is quite consistent with $\rho \approx -2.2$ for this conversion of anilines.

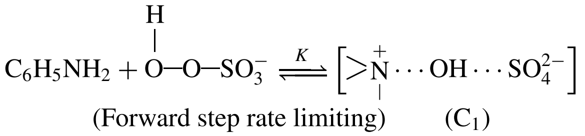
Table V Reaction Constant Values at Different Temperatures

Correlation	Temperature (°C)	ρ	n
$\rho\sigma$	20	−2.27	17[a]
	30	−2.21	
	40	−2.27	
$\rho\sigma$	20	−2.19	11[b]
	30	−2.15	
	40	−2.12	
$\rho\sigma^+$	20	−1.60	11[b]
	30	−1.57	
	40	−1.56	
$\rho\sigma$	20	−2.49	7[c]
	30	−2.48	
	40	−2.42	
$\rho\sigma^+$	20	−1.72	7[c]
	30	−1.71	
	40	−1.69	
$\rho\sigma^-$	20	−1.69	7[c]
	30	−1.68	
	40	−1.64	

[a] *o*-COOH not included in correlation since σ_o^* values are not available.

[b] Effect of *meta*- and *para*-substituents in the correlation.

[c] Effect of *para*-substituents only in the correlation.



$$C_6H_5NH_2 + \overset{\overset{\displaystyle H}{|}}{O}{-}O{-}SO_3^- \underset{}{\overset{K}{\rightleftharpoons}} \left[>\overset{+}{\underset{|}{N}} \cdots OH \cdots SO_4^{2-} \right]$$

(Forward step rate limiting) (C_1)

(6)

$$C_1 \xrightarrow[\text{Fast}]{k_2} C_6H_5NHOH + HSO_4^- \quad (7)$$

$$C_6H_5NHOH \xrightarrow[\text{Fast}]{HSO_5^-} C_6H_5NO + H_2O + HSO_4^- \quad (8)$$

The transition state C_1 with a positive charge on nitrogen is consistent with significant kinetic electronic substituent effects. The proposed mechanism is well supported by the observed stoichiometry of 2:1 for HSO_5^- : amine.

Negative entropies of activation are as expected for a bimolecular reaction [15]. It also implies highly organized or rigid transition state. The linearity of the plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ is a criterion for validity of the Hammett equation [16]. As is clear in the isokinetic plot of Fig. 8, there is a considerable scattering of points. Exner [17] criticized the validity of such linear correlations between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as these quantities are dependent on each other. The linear relationship in the Exner plots log k_{obs}(40°C) versus log k_{obs} (30°C) (Fig. 8, $r \approx 0.998$; $s \approx 0.601$) supports a similar mechanism for all the anilines listed. The isokinetic temperature β was calculated using the relation [17],

$$\beta = \frac{T_1 T_2 (1 - f)}{(T_1 - T_2 f)}$$

where f is slope of the Exner plot. The β value is found to be less than the experimental temperature (<200 K).

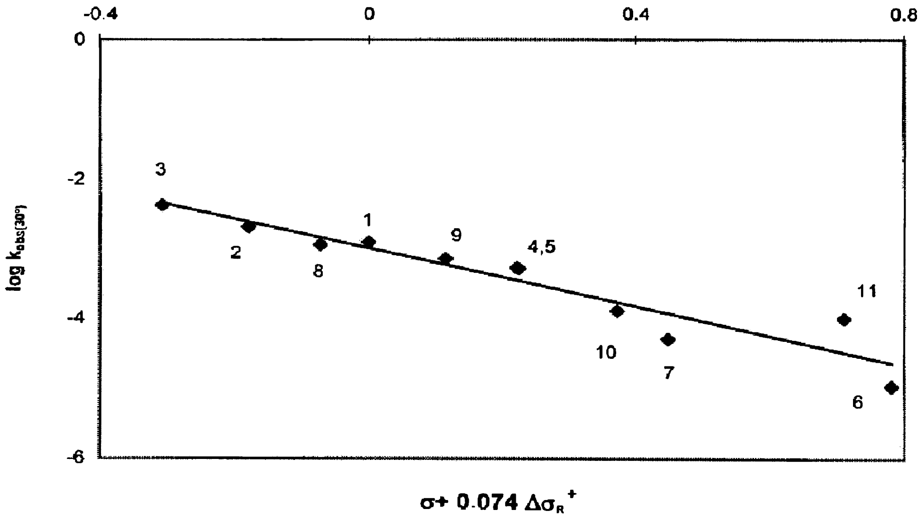


Figure 6 Yukawa–Tsuno plot (numbered as in Table IV).

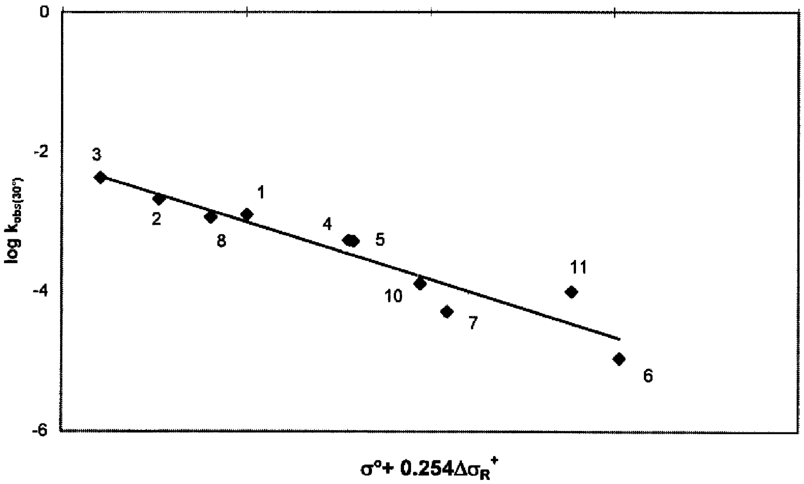


Figure 7 Yukawa–Tsuno plot (numbered as in Table IV).

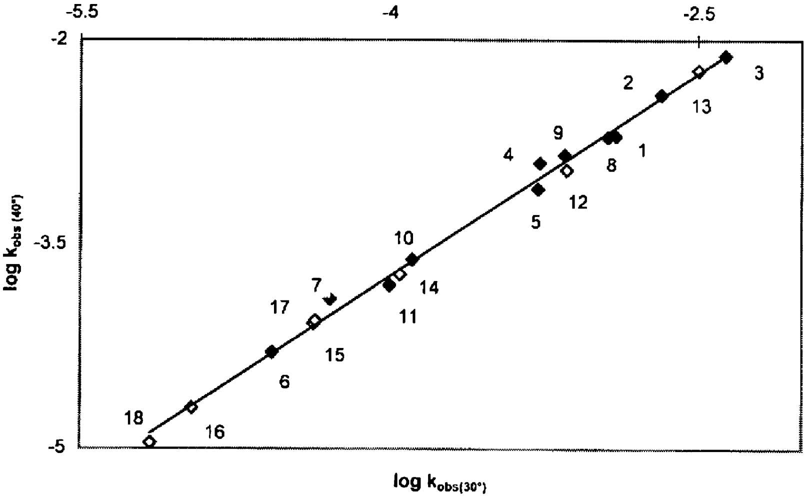


Figure 8 Exner plot (numbered as in Table IV). ♦ *m*— and *p*—substituents. ◇ *o*— substituent.

Table VI Yukawa–Tsuno Analysis

No.	Substituent Constants	Temp. (°C)	100R	SE	ψ	f	n
1	$\sigma, (\sigma^+ - \sigma)$	20	94.88	0.278	0.370	0.166	11
		30	94.96	0.270	0.368	0.165	11
		40	95.82	0.242	0.336	0.190	11
2	$\sigma^0, (\sigma^+ - \sigma^0)$	20	95.02	0.290	0.372	0.175	10
		30	95.11	0.283	0.369	0.174	10
		40	96.02	0.252	0.334	0.156	10
		para-Substitutents only					
3	$\sigma, (\sigma^+ - \sigma)$	20	97.33	0.262	0.304	0.167	7
		30	97.96	0.226	0.265	0.145	7
		40	98.00	0.220	0.263	0.144	7
4	$\sigma^0, (\sigma^+ - \sigma^0)$	20	96.94	0.280	0.325	0.179	7
		30	97.62	0.244	0.287	0.157	7
		40	97.88	0.226	0.271	0.148	7
5	$\sigma, (\sigma^- - \sigma)$	20	99.63	0.098	0.114	0.061	7
		30	99.70	0.087	0.102	0.055	7
		40	99.80	0.069	0.083	0.044	7
6	$\sigma^0, (\sigma^- - \sigma^0)$	20	99.73	0.084	0.097	0.052	7
		30	99.70	0.087	0.102	0.055	7
		40	99.80	0.070	0.085	0.045	7

Since β–T is negative, the reaction is believed to be entropy controlled. The $\Delta S^{\neq}$ values are similar to the corresponding data measured for typical reactions involving oxygen transfer [2,18].

Substituent effects in the conversion of anilines to nitroso products are different in various solvents. Abdul and Maruthamuthu in their recent kinetic study [3] on the effect of substituents on the rate of the reaction between aromatic amines and peroxomonosulfate ion in aqueous acetic acid medium have reported that both electron-releasing and withdrawing groups retard the reactivity. No simple Hammett relation is found for the substituent effects. The results are explained by the formation of a transition complex of cyclic nature. Effect of substituents on the reactivity of anilines by HSO_5^- [1] revealed interesting results in basic medium (pH > 11). In a typical Michaelis-Menten type kinetics, contrasting kinetic behaviors are observed for the effect of substituents on the formation constant (K) of the radical cation intermediate, $PhNH_2$, and its rate of decomposition (k). Ru(III)-inhibited oxidation of anilines by HSO_5^- [2] to nitroso products in acidic solution (pH ≈ 2.6) resulted in the formation of a concave upward Hammett plot with a rate minimum. In contrast to previously described results, in the present investigation, the aniline–$HOOSO_3^-$ reaction system in aqueous MeCN medium obeys the Hammett and Yukawa relationships. It appears the contrasting effect of the substituents in the conversion of anilines to nitroso products depends on the nature of the solvent. The kinetics of oxidation of anilines [19] by $H_2PO_5^-$ in aqueous acetonitrile medium at pH 5.4 revealed that all the *meta*- and *para*-substituted anilines except the *p*-nitro one are on the Hammett line. The rates of *ortho*-substituents, which are consistently retarded, form a separate line.

Table VII The Ratio of Rate Coefficients of *para* and *ortho* Substituents

	k_p/k_o		
Substituent	20°C	30°C	40°C
CH_3	2.61	2.97	2.78
OCH_3	1.48	1.36	1.31
Cl	13.80	12.56	15.10
COOH	0.96	1.16	1.46
NO_2	1.50	1.57	1.82

EXPERIMENTAL

The reactions were carried out in 80% aqueous acetonitrile (v/v) medium. All the solutions were kept in a thermostat at constant temperature controlled using a Gallenkemp thermostat to an accuracy of ±0.1°. The measurements were made between 293 K and 313 K. The required volumes of these solutions for each run were mixed, and 2 mL aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 mL of 2% potassium iodide solution and the liberated iodine was titrated against standard thiosulfate to a starch end point.

Stoichiometry and Product Analysis

The stoichiometric runs carried out in the presence of excess of oxone at 30°C, revealed that two moles of the oxidant react with 1 mole of aniline. The reaction between oxone and aniline under the kinetic conditions gave an insoluble residue after standing for 3 h. The recrystallised (in alcohol) residue was found to be nitrosobenzene as established by determining the melting point (mp 60–61°C), which corresponds to the literature value. Similar nitroso products were obtained for the *meta*-, *para*-, and *ortho*-substituted anilines. The products were confirmed by TLC, m.p., and NMR data in comparison with the authentic sample.

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